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Determination of trace amounts of phosphorus in terephthaloyl chloride by d.c. polarography

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A method is described for the determination of trace amounts of phosphorus present in terephthaloyl chloride (TCL). Phosphorus was extracted from the sample by distilled water. It was converted into molybdophosphoric acid, extracted with *n*-butyl acetate and molybdenum in the organic extract determined by catalytic polarography. Charging current compensation was employed to improve precision and detecton limit. The method enabled the determination of 0.0005% P in TCL and the relative standard deviation was 4.2%.

Aramid fibre has proven to be an excellent fibre for the reinforcement of plastics and has gained acceptance in many aircraft applications. Composites of aramid fibres are now used in non-structural and semi-structural components in aerospace vehicles, commercial and business aircrafts, and helicopters to achieve weight savings, stiffness and strength. Polyparaphenylene terephthalamide (PPTA) is a raw material used for the preparation of aramid fibre. PPTA in turn is prepared from terephthaloyl chloride (TCL) which is obtained[1] by the reaction of terephthalic acid with PCl_5. The phosphorus residues in TCL are removed by distillation and recrystallisation since the presence of phosphorus in TCL leads to unwanted side reactions in the preparation of PPTA, and the concentration of residual phosphorus in TCL should be less than 0.003% (ref.2). Hence, after purification of TCL, the phosphorus content of TCL has to be determined in order to decide whether further purification is necessary or not. This requires an analytical method for the determination of phosphorus in terephthaloyl chloride at very low concentration levels. When the phosphorus concentration in the sample is more than 0.005% (0.05 μg/mg), spectrophotometric method based on molybdenum blue could be used for phosphorus determination[3]. However, when the phosphorus concentration in the sample is lower than 0.005%, there is a need for a method with much higher sensitivity. We had reported earlier, a sensitive polarographic method for phosphorus determination, by combining two different methods of improving the sensitivity[4]. In that method, phosphorus was converted into phosphomolybdic acid complex, isolated by selective solvent extraction and the molybdenum content of the organic extract determined by catalytic d.c. polarography. The suitability of this approach for phosphorus determination in terephthaloyl chloride is discussed in this paper.

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Experimental Procedure

Instrumentation

The polarograph used charging current compensation and has been described earlier[5]. A Metrohm polarographic cell with a mercury pool as counter electrode and an SCE as reference electrode was used with a 3-s Sargent capillary, the drop-time being kept at 0.5 s by an electromechanically controlled knocker. The water jacketed polarographic cell was maintained at 34 ± 0.1 °C. Solutions were purified by passage of purified hydrogen for 20 min.

Reagents

Double distilled water was used and the reagents used were of analytical grade.

Standard phosphorus solution (25 μg/mL) — Dissolve 0.0929 g of ammonium-di hydrogen phosphate in 1 L of distilled water.

Wash solution for phosphorus — Equilibrate 2 *M* hydrochloric acid with *n*-butyl acetate (or *i*-butyl acetate), then discard the organic phase.

Supporting electrolyte — Dissolve 85 g of sodium nitrate in 0.25 *M* sulphuric acid and dilute to 1 litre with the same acid. Ammonium heptamolybdate tetrahydrate solution, 5%.

Solvent for extraction — *n*-butyl acetate (or *i*-butyl acetate) and cyclohexane.

Procedure — Take one gram of well powdered terephthaloyl chloride sample in a 100 mL beaker and add about 40 mL of distilled water and slowly heat on a sand bath till the volume reduces to about 25 mL cool. Filter through a Whatman No.1 filter paper, wash with 15 mL of distilled water and make up the solution to 50 mL.

Determination of phosphorus —In three different 60 mL separatory funnels take respectively, 10 mL of distilled water, 10 mL of the sample solution and 10 mL of the sample solution plus 3.0 µg of phosphorus solution as the standard addition. To each add 2 mL of 5% ammonium molybdate solution, adjust to *p*H 0.7 with dilute nitric acid and let stand for 10 min. Add 10 mL of *n*-butyl acetate to each of the separatory funnels and shake the funnels for 1 min. When the phases have separated, discard the lower aqueous layers. Add 2.0 mL cyclohexane to each and wash the organic layers three times with 10 mL portions of phosphorus wash solution (shaking for 30 s for each wash) and discard the washings. Add 10 mL of 0.5 *M* sodium hydroxide solution to the organic layers and shake for 1 min. When the phases have separated, collect the lower layers in different 50 mL standard flasks. To each add 6.7 mL of 2.3 *M* sulphuric acid and 4.25 g of sodium nitrate and make up to the mark. Determine the molybdenum content of these solutions by adding 4 mL of each of these stripped solutions to 20 mL of supporting electrolyte and record the polarograms. Subtract the blank value and determine the phosphorus content of the sample by the method of standard addition.

If *i*-butyl acetate is used for the extraction of MPA instead of *n*-butyl acetate, do not add cyclohexane to the organic phase; otherwise the procedure is identical to what is described above.

Results and Discussion

The rationale for choosing the nitrate/sulphuric acid medium for the catalytic polarographic determination of molybdenum has been described in our previous paper[4]. For the formation of the MPA complex, a *p*H of 0.7 was chosen and 2 mL of 5% ammonium molybdate was added as the optimum amount of the reagent in accordance with what has been reported earlier[4]. For the extraction of MPA *i*-butyl acetate and *n*-butyl acetate were systematically investigated. From a review of the literature[6,7] it is seen that *i*-butyl acetate is one of the best solvents for MPA extraction. But, to the best of our knowledge, *i*-butyl acetate is not commercially available in our country whereas *n*-butyl acetate is readily available and which is also recommended in literature for MPA extraction. In an AAS study of the extractability of binary heteropolymolybdic acids Simon and Boltz investigated five different solvent for the extraction of MPA and concluded that the highest distribution ratio was obtained for *n*-butyl acetate and methyl isobutyl ketone[8]. Similarly Bernal *et al.*[9] in an indirect AAS method for the determination of phosphorus in aluminium alloys investigated several solvents for the extraction of MPA and concluded *n*-butyl acetate as the best solvent for MPA extraction. No comparative study of these two solvents for MPA extraction has been reported in literature and hence this aspect was undertaken in this study.

In order to improve the overall detection limit it is essential to minimise the magnitude of the blank which is due to the simultaneous extraction of isopolymolybdic acid (IPMA). We observed that the magnitude of the blank for *n*-BuOAc extraction is higher than that of *i*-BuOAc extraction. Generally an acidic wash is given to the organic layer to minimise the blank. We undertook a systematic study to decrease this blank further. Following our earlier work on the use of hydrocarbon addition to the organic extract before giving an acidic wash[4], we added cyclohexane to the *n*-BuOAc extract containing MPA and then washed it three times with 12 mL of 2 *M* HCl. This approach had a profound effect in decreasing the blank as shown in Fig.1. It is seen that the addition of 2 mL of cyclohexane to the organic layer containing MPA and then three washes each with 12 mL of 2 *M* hydrochloric acid was optimal for *n*-BuOAc extraction. Benzene, cyclohexane, toluene and xylene were investigated as the hydrocarbon and the most favourable signal-to-blank ratio (SBR) was obtained when benzene or cyclohexane was added to the organic phase.

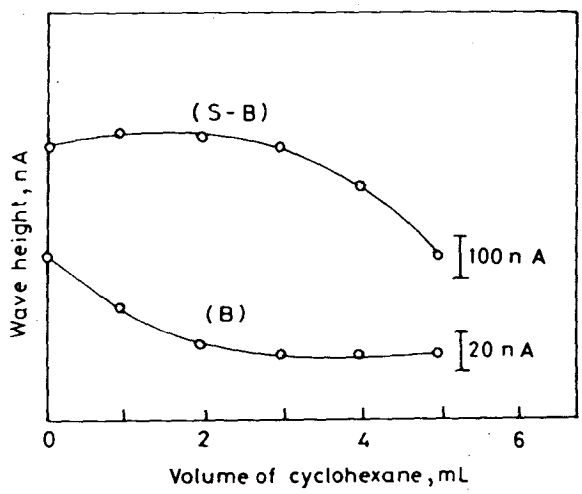

Fig. 1—Variation of blank and blank corrected sample wave heights for 18.2 µg/L phosphorus with variation in the amount of cyclohexane added to the *n*-BuOAc phase containing MPA

For *i*-butyl acetate extraction the magnitude of the blank was almost negligible and much lower than what was obtained for *n*-BuOAc extraction, and the signal-to-blank ratio did not improve further by the addition of hydrocarbon as shown in Fig.2. It is seen that while the blank-corrected-sample-wave heights (S-B) steadily decreased, the wave heights of the blank remained unaltered with the addition of hydrocarbon. Hence three washes with 10 mL of 2 *M* HCl alone was sufficient to get the most favourable SBR.

Calibration graphs for phosphorus determination were prepared by using these two solvents to evaluate the sensitivity. Use of *i*-BuOAc offered a sensitivity of 80 nA. L μg^{-1} and that of *n*-BuOAc 34.5 nA. L μg^{-1}. Hence it is always preferable to use *i*-butyl acetate for phosphorus determination. Neverthless the sensitivity offered by *n*-BuOAc is good enough for practical applications. In this report we demonstrate the use of *n*-BuOAc for phosphorus determination in terephthaloyl chloride since, as mentioned earlier, *n*-BuOAc is easily available whereas *i*-BuOAc is not.

Suitability of the method for the determination of phosphorus in terephthaloyl chloride — Fig.3 shows the polarograms obtained for the determination of phosphorus by the method of standard addition in a particular sample of terephthaloyl chloride and the phosphorus concentration was determined to be 0.0017%. The polarograms of the sample, blank and standard addition are seen to be well defined. The initial and final portions of the polarograms are almost parallel to the X-axis because of the efficient removal of charging current by CCC.DC polarograph.

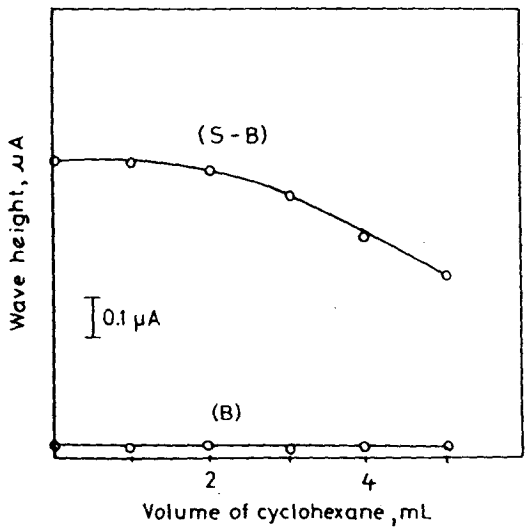

Fig. 2—Variation of blank and blank corrected sample wave heights for 18.2 μg/L phosphorus with variation in the amount of cyclohexane added to the *i*-BuOAc phase containing MPA

From Fig.3c it can be seen that the leaching of phosphorus in TCL takes place in a single step by the recommended procedure. Here, to the TCL residue after leaching phosphorus, another 50 mL of water was added and leached again and made up to 50 mL. The phosphorus content of this solution was determined by taking 10 mL and applying the procedure. It gave the same waves height as that of the blank indicating that quantitative leaching of phosphorus in TCL sample takes place in a single step extraction. In order to examine whether any nonextractable phosphorus is present in the residue, the residue was ashed in a platinum crucible by heating to 900°C and the contents dissolved in hot HNO_3/H_2SO_4. This solution did not contain any phosphorus thus establishing that the leaching procedure recommended is quantitative.

Table 1 summarises the results obtained for the determination of phosphorus in certain TCL samples synthesised in our laboratory. The results were cross-checked by spectrophotometry for certain TCL samples and are also given in Table 1. It is seen that there is good agreement between the present method and spectrophotometry.

Detection limit — The detection limit was evaluated by using the expression[10],

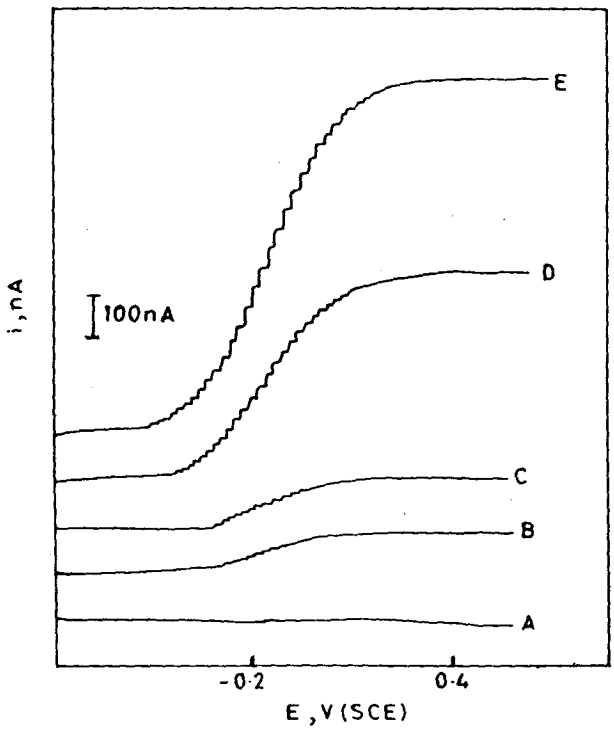

Fig. 3—Polarograms obtained for the determination of phosphorus in a particular sample of terephthaloyl chloride (with P = 0.0017%) by the method of standard addition. (A) Supporting electrolyte alone; (B) Reagent blank; (C) Polarogram of the second extract; (D) Polarogram due to the presence of 0.0017% P in TCL sample; (E) "D" + 3.0 μg of phosphorus as standard addition

Table 1 Determination of phosphorus in terephthaloyl chloride by polarography and spectrophotometry

Sample No.	Percentage phosphorus	
	Polarography (present method)	Spectrophometry (molybdenum blue method[3])
1	0.0017	–
2	0.0033	–
3	0.0045	0.005
4	0.0053	0.005
5	0.0162	0.016

$$C_L = 3\sigma/S$$

where C_L is the minimum detectable concentration, σ is the standard deviation of the blank (= 14.5 nA) and S is the sensitivity of the method (= 34.5 nA. L μg^{-1}). The detection limit was found out to be 1.26 µg/L phosphorus in the final solution. For the procedure recommended in this report this value would correspond to 0.00019% P in TCL sample. The detection limit for phosphorus using *i*-BuOAc extraction was evaluated to be 0.3 µg/L in the final solution (σ = 8.3 nA and S = 80 nA. L μg^{-1}). This value would correspond to 0.00005% P in TCL sample. The relative standard deviation (eight determinations) was 4.2% (for 0.0017% P in TCL samples).

Interference studies — Foreign ions may interfere at two stages: in the formation and extraction of the HPMA, and in the polarography. These have been already studied and confirmed by our observations[4]. Besides, terephthaloyl chloride used in this study was of high purity and *n*-butyl acetate and *i*-butyl acetate are highly selective for the extraction of MPA and hence none of the ions present in the sample or the reagents used in the procedure caused any interference.

Conclusion

A highly sensitive and selective polarographic method has been reported in this investigation for the determination of trace amounts of phosphorus in terephthaloyl chloride. The method developed here, incorporating the improved sensitivity of the catalytic wave of molybdenum, the improved precision by the use of CCC. DC polarograph for recording the polarogram, and the suitable post-extraction treatment to the organic extract containing MPA to minimise the blank enables the determination of phosphorus in TCL samples at 0.0005% levels (on the assumption that the practical determination limit is 10-times the inherent detection limit of the method).

Acknowledgement

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